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ICP Analysis for Trace Elements by SW-846 Method 6010C/D

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1.0 Scope and Application

1.1 This procedure describes the analysis of trace elements including metals in solution by Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICPAES). This procedure references Methods 6010C and 6010D for hazardous waste (RCRA) testing.

1.2 The elements that can be determined by this procedure are listed in Attachment 1, together with the routine reporting limits. Additional elements may be analyzed under Method 6010C and 6010D provided that the method performance criteria presented in Section 12.0 are met.

1.3 The laboratory digests all water samples according to SOP DV-IP-0010.

1.4 Silver concentrations must be below 1.0 mg/L in aqueous sample digestates and 100 mg/kg in solid matrix sample digestates. Precipitation may occur in samples where silver concentrations exceed these levels and lead to the generation of erroneous data. Samples with silver concentrations exceeding these levels must be re-prepared and reanalyzed using a smaller sample amount.

1.5 The digestion procedure for soil samples is described in SOP DV-IP-0015.

1.6 State or client specific requirements may take precedence over this SOP for water analyses. Review special instructions for each project before starting work.

2.0 Summary of Method

2.1 The laboratory uses simultaneous ICPAES instruments, with both axial and radial viewing configurations. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs.

2.2 Characteristic atomic-line emission spectra are produced by a radio frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the emission lines are monitored by a charge injection device (CID). The photo-currents from the charge injection device (CID) are processed and controlled by a computer system.

2.3 A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interferences and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result.

2.4 Refer to the appropriate SOPs for details on sample preparation methods: DV-IP-0010 for aqueous samples and DV-IP-0015 for soil samples.

3.0 Definitions

3.1 Dual View ICP – an ICP equipped with both radial and axial viewing capabilities.

3.2 Dissolved Metals - Those elements which pass through a 0.45-μm membrane. The sample is acidified after filtration.

3.3 Potentially Dissolved Metals - Potentially dissolved metals is the concentration of metals in solution after acidifying the sample with nitric acid to pH <2, holding at room temperature for 8 to 96 hours, and then filtering through a 0.45-μm membrane filter. This definition is based on the Colorado surface water regulations.

3.4 Suspended Metals - Those elements which are retained by a 0.45-μm membrane.

3.5 Total Metals - The concentration determined on an unfiltered sample following vigorous digestion.

3.6 Total Recoverable Metals - The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid.

3.7 Reporting Limit (RL) - The lowest concentration to which results are reported without qualification. Details concerning RLs are presented in Policy DV-QA-009P.

3.8 Reagent Water - Water with a resistivity of 1 Megohm-cm or greater. The TestAmerica Denver deionized water supply meets this requirement with a resistivity of at least 10 Megohm-cm.

3.9 Refer to the Glossary of the TestAmerica Denver Quality Assurance Manual (QAM) and Policy DV-QA-003P, *Quality Control Program*, for definitions of general analytical and QA/QC terms.

4.0 Interferences

4.1 Spectral, physical, and chemical interference effects may contribute to inaccuracies in the determinations of trace elements by ICP. Spectral interferences are caused by the following:

4.1.1 Overlap of a spectral line from another element.

4.1.2 Unresolved overlap of molecular band spectra.

4.1.3 Background contribution from continuous or recombination phenomena.

4.1.4 Stray light from the line emission of high concentration elements.

4.2 A background correction technique is used to compensate for variable background contribution to the determination of trace elements. Background correction is not required in cases where a background corrective measurement would actually degrade the analytical result.

4.3 Spectral Interferences

Inter-element correction factors (IECs) are necessary to compensate for spectral overlap. Inter-element interferences occur when elements in the sample emit radiation at wavelengths so close to that of the analyte that they contribute significant intensity to the analyte signal. If such conditions exist, the intensity contributed by the matrix elements will cause an excessively high (or sometimes low) concentration to be reported for the analyte. Inter-element corrections must be applied to the analyte to compensate for the effects of these unwanted emissions.

4.4 Physical Interferences

An internal standard (IS), yttrium or other suitable element, is added to all solutions to correct and monitor physical interferences. Use of a peristaltic pump and the mass flow controller also help to overcome physical interferences. Physical interferences are generally considered to be effects associated with sample transport, nebulization, and conversion within the plasma. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension), or during excitation and ionization processes within the plasma itself. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If internal standard recoveries are not acceptable (see Section 9.11), then dilution of the sample may be necessary to overcome the interferences.

4.5 Chemical Interferences

Chemical interferences are characterized by molecular compound formation, ionization effects, and solute vaporization effects. Normally these effects are not significant with the ICP technique, but if observed, can be minimized by buffering the sample, matrix matching, or standard addition procedures.

5.0 Safety

5.1 Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2 This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, nitrile or latex gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.3 Specific Safety Concerns or Requirements

5.3.1 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile or latex gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be

removed and discarded; non-disposable gloves must be cleaned immediately.

5.3.2 The ICP plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma. The RF Generator produces strong radio frequency waves, most of which are unshielded. People with pacemakers should not go near the instrument while in operation.

5.4 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material [(1)]	Hazards	Exposure Limit[(2)]	Signs and Symptoms of Exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions. 2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

6.1.1 Thermo Fischer ICP 6500E Trace Analyzers are currently used.

Instruments with demonstrated equivalent performance can also be used

6.1.2 Radio Frequency Generator

6.1.3 Argon gas supply

6.1.4 Coolflow or appropriate water-cooling device.

6.1.5 Peristaltic Pump.

6.1.6 Autosampler.

6.2 Supplies

6.2.1 Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.2.2 Class A volumetric flasks.

6.2.3 Autosampler tubes.

6.3 Computer Software and Hardware

Please refer to the master list of documents and software located on R:\QA\Read\Master List of Documents\Master List of Documents, Software and Hardware.xls or current revision for the current software and hardware to be used for data processing.

7.0 Reagents and Standards

7.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. All standards used in calculations shall be entered into the TALS Reagent Module with all applicable information (e.g., components, concentrations, expiration, etc.).

7.2 Shelf-Life

7.2.1 Stock standards, standards as received from the vendor, expire on the date assigned by the vendor. If no date is assigned by the vendor, a one-year expiration will be assigned by the laboratory.

7.2.2 The expiration date of intermediate concentration standards or working standards will be set at six months or less and cannot be later than the date assigned to any of the stock standards used to prepare the intermediate solution.

7.2.3 If visible deterioration is noted for any standard, it must be re-verified against a second-source. Any standard that does not verify must be replaced immediately.

7.3 Standards

7.3.1 Standards used for calibration and quality control purposes must be NIST traceable, where available. Multi-component custom blend standards must be verified against a second-source standard before they are first put into use (the only exception is standards purchased directly from NIST), as described in SOP DV-QA-0015. If the standard has been purchased previously it does not need to be verified, but the COA must be inspected to confirm that there have been no changes to the standard analyte levels.

7.3.2 Stock standards are purchased as custom multi-element mixes or as single-element solutions. All standards must be stored in FEP fluorocarbon, polyethylene, or polypropylene bottles. Silver standards must be protected from light. The preparation frequency is governed by the parent standard with the earliest expiration date unless specified otherwise in this SOP. Detailed instructions regarding the preparation of standards and reagents are given in this section. Alternate procedures are allowed as necessary to accommodate volume requirements as long as final concentrations are maintained and an accurate description of the standard or reagent used is entered into the Reagent Module in the TestAmerica LIMS TALS.

7.3.3 Intermediate calibration and QC standards are prepared in water with hydrochloric and nitric acids in order to approximate the acidic matrix of the various digests analyzed. This is an important point. Even with the use of yttrium as an internal standard, deviations from these concentrations can cause physical effects, as discussed in Section 4.4 of this procedure.

7.4 Reagent Blank / Initial Calibration Blank (ICB) / Continuing Calibration Blank (CCB)

Fill a 20-liter carboy with about 18 liters of reagent water. Slowly add 1 liter of concentrated nitric acid and 1 liter of concentrated hydrochloric acid. Adjust the total volume to 20 liters. Mix carefully. Record the acid lot number and other required information in the Blank Reagent Logbook stored in the metals prep area.

7.5 Stock ICSA and ICSAB Standards

The following standards are purchased from commercial sources:

Stock ICSA & ICSAB Standard	Elements	Concentration (mg/L)
Icp stk ICSA	Fe Al, Ca, Mg	2,000 5,000
ANALYTES B	Ba, Be, Co, Cr, Cu, Mn, V Ag, Cd, Ni, Pb, Zn	50 100
ICP ISAB STD1	Li, Mo, Sb, Sr As, B, P Se K, Na	100 200 500 5,000

Stock ICSA & ICSAB Standard	Elements	Concentration (mg/L)
ICP ISAB STD2	Ti Sn	100 1,000
10000 Si	Si	10,000
10000 Th	Th	10,000
1000 Tl	Tl	1,000
1000 Zr	Zr	1,000
1000 S	S	1,000
1000 Bi	Bi	1,000

7.6 ICSA Working Standard (ICP ICSA)

A combined working ICSA standard is made in a 250-mL volumetric flask using the following volumes of the Stock ICSA and ICSAB Standards:

Stock Standard	Volume of Stock Added (mL)
ICSA Std	25

Adjust to volume (250 mL) using the reagent blank solution. This produces the final ICSA standard concentrations shown in Attachment 4.

7.7 ICSAB Working Standard

A combined working ICSAB standard is made in a 250-mL volumetric flask using the following volumes of the Stock ICSAB Standards:

Stock Standard	Volume of Stock Added (mL)
Icp stk ICSA	25
ANALYTES B	2.5
ICP ISAB STD1	2.5
ICP ISAB STD2	2.5
10000 Si	0.25
10000 Th	0.05
1000 Tl	2.5
1000 Zr	0.25
1000 S	0.25
1000 Bi	0.25

Adjust to volume (250 mL) using the reagent blank solution. This produces the final ICSAB standard concentrations shown in Attachment 4.

7.8 Calibration Check Standard (S1, S2)

The two calibration check standards are the same as the working ICAL standards (ICP ICAL1A and ICP ICAL2A) described in Section 7.12.

7.9 Laboratory Control Sample (LCS) Stock Standards

The LCS stock standards are purchased from commercial sources. The stocks are custom-made standards purchased at ready-to-use concentrations as follows:

LCS Stock Standards	Elements	Concentration (mg/L)
ICP SPK 3A	Ca, K, Mg, Na P Al, Ba, Bi, Se, Tl, U, As, Fe, Li, Sr, Th Co, Mn, Ni, Pb, V, Zn Cu Cr Cd Ag, Be	5,000 1,000 200 100 50 25 20 10 5
ICP SPK 2B	Sb, Zr B, Mo, Ti Sn Si (SiO_2) S	50 100 200 1,000 (2,140) 200

The soil and water LCSs are prepared according to the instructions in SOPs DV-IP-10 and DV-IP-0015. Final concentrations are shown in Attachment 2.

7.10 Matrix Spike / Matrix Spike Duplicate (MS/MSD)

The same LCS stock standards described in Section 7.9 are also used to prepare matrix spikes and matrix spike duplicates. Final concentrations are shown in Attachment 2.

7.11 Post Digestion Spike (PDS) Standards (Analyte Addition Spike Standards)

The custom standards tabulated below are purchased from a commercial source. Add 0.06 mL of each to 6 mL (100X) of digestate or dilution of digestate.

PDS Stock	Elements	Conc. (mg/L)
ICP PDS 1	Ag, Be, Cd, Co, Cr, Cu, Mn, Ni, Sr, V Ba, Li, Pb, As, Se, Th, Tl, Zn U Al, Fe P Ca, K, Mg, Na,	5 5 10 20 50 100 200 2,000
ICP PDS 2	Mo, Ti, Zr B, Sb, Sn Si (SiO_2)	5 10 500 (1,070)

7.12 Initial Calibration (ICAL) Standards

7.12.1 Stock Calibration Standards

The following stock solutions are purchased from commercial sources.

Stock Standard	Elements	Conc. (mg/L)
Icp cal std 2	Mo, Ti, Zr Sn Si (SiO_2)	100 200 1,000 (2,140)
Icp cal std 3	Ag, Al, B, Ba, Be, Cd, Co, Cr, Cu, Mn, Ni, Sr, V, Zn Li, P Fe Ca, Na Mg K	100 200 500 1,000 4,000 10,000
Al, Ca, Fe, Na, S, Th Stocks	Al, Ca, Fe, Na, S, Th	10,000
As, Pb, Sb, Se, Tl, U, Bi Stocks	As, Pb, Sb, Se, Tl, U, Bi	1,000

7.12.2 Working Initial Calibration Standard (ICP ICAL1A)

Add 10.0 mL each of Icp cal std 2 and Icp cal std 3 to a 1L volumetric flask partially filled with reagent blank solution. Add 2 mL of the As, Pb, Sb, Se, and Tl stocks. Dilute to the mark with reagent blank solution.

7.12.3 Working Initial Calibration Standard (ICP ICAL2A)

Add 10 mL of the Al and Fe and 50 mL of the Na 10,000 mg/L stock solutions; 1 mL of the Th and 20 mL of the U 1,000 mg/L stock solutions; 2 mL of the 1,000 mg/L Bi solution and 1 mL of the 10,000 mg/L S solution to a 1,000-mL volumetric flask partially filled with reagent blank and dilute to the mark with reagent blank.

7.13 Initial Calibration Verification (ICV)

7.13.1 ICV Stock Standards

The following stock solutions are purchased from commercial sources:

Stock Standard	Elements	Conc. (mg/L)
Icp ICVL A	Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Li, Mn, Ni, Pb, Sr, V, Zn Se, Tl Ca, Na Mg K	25 50 200 1,000 2,000

Stock Standard	Elements	Conc. (mg/L)
Icp ICVL B	Ag, Mo, Sb, Ti, Zr Sn P, Si (SiO_2)	25 50 200 (428)
Icp ICVH	Al, Na Fe U Th	4,000 8,000 500 300
Bi, S Stocks	Bi, S	1,000

7.13.2 Working High Initial Calibration Verification (ICP ICVH)

Add 1.0 mL of the ICVH Stock, 0.05 ml Bi and 0.4 mL of the Sulfur to a 100 mL volumetric flask partially filled with reagent blank solution and dilute to the mark.

Note: For Method 6010D the ICV working solutions must be prepared daily.

7.13.3 Working Initial Calibration Verification (ICP ICV)

Add 1.0 mL of each of the Icp ICVL A and Icp ICVL B stock solutions to a 100-mL volumetric flask partially filled with reagent blank solution and dilute to the mark.

Note: For Method 6010D the ICV working solutions must be prepared daily.

7.14 Reporting Limit Standard (RLSTD)

7.14.1 RL Stock Standard

The following stock solutions are purchased from commercial sources:

Standard	Elements	Conc. (mg/L)
ICP RLSTD 1A	As, Sb, Se, Tl Pb	10 3
ICP RL STD 2A	Mo, Ti, Zr Sn Si (SiO_2)	10 20 500 1,070
ICP RL STD3A	Ag, Cr, Cu, Li, Ni, Th, V, Zn, Al, B Ba, Cd, Co, Sr Be Ca, Mg Fe K, Na, P Mn U	10 100 5 1 200 30 1,000 3 60
100 mg/L S	S	100

Standard	Elements	Conc. (mg/L)
100 mg/L Bi	Bi	100

7.14.2 Daily Reporting Limit Standard (ICP CRI)

Add 0.1 mL of each of ICP RLSTD 1A, ICP RL STD 2A, ICP RL STD 2A, 100 mg/L Bi and 100 mg/L S to a 100-mL volumetric flask partially filled with reagent blank and dilute to the mark. The Working RL standard must be prepared fresh each day.

7.15 High Continuing Calibration Verification (ICP CCVH)

Perform a 2x dilution of the working ICP ICAL2A solution (Section 7.12.3) with reagent blank solution.

7.16 Continuing Calibration Verification (ICP CCV)

Perform a 2x dilution of the working ICP ICAL1A solution (Section 7.12.2) with reagent blank solution.

7.17 Low Level ICV/Low Level CCV (ICP LLCCV)

The low level ICV/CCV verification stock standards are custom-made commercial standards as follows:

LLICV/LLCCV Stock Standard	Elements	Conc. (mg/L)
ICP LLCCV-1	K	300
	Na	100
	Ca, Mg	20
	Al, Bi, Fe	10
	U	6
	Ni	4
	Zn	2
	As, Cu, Se, Tl, Th	1.5
	Ba, Cr, Co, Li, Mn, Ag, Sr,	1
	V	1
	Pb	0.9
	Cd	0.5
	Be	0.1
ICP LLCCV-2	P	300
	Si	50
	B	10
	Sn	10
	Mo	2
	Zr	1.5
	Sb	1
	Ti	1

7.17.1 Low Level ICV \ Low Level CCV, Working Standards

RL Standard	Vol. of Stock Added (mL)
ICP-LLCCV-1	1
ICP-LLCCV-2	1

Adjust to volume (100 mL) using the reagent blank solution.

7.18 Linear Range Verification Standard (LR)

The LRA standard is prepared from single element stock standards of each metal obtained from a commercial source. The stock standards are each purchased at a concentration of 1,000 mg/L except for Iron and Silicon which are each at a concentration of 10,000 mg/L. The LRA is prepared by taking the appropriate volume of each stock and adding it to a 500 mL volumetric flask partially filled with reagent blank and diluted to the mark after all elements have been added. The volume of each stock solution of each metal and volume used, along with final concentrations of each are listed in the following table.

Elements	Stock Conc. (mg/L)	Volume of stock (mL)	Final Conc. (mg/L)
Cd,	1,000	1.0	2
Co, Mo, Se, Tl	1,000	2.5	5
As, B, Cr, Cu, Mn, Ni, Pb, Sr, Ti, V, Zn	1,000	5.0	10
Ba	1,000	6.0	12
Fe	10,000	25	500
Si (SiO_2)	10,000	2.5	50 (107)

7.19 Reagents

7.19.1 Concentrated nitric acid (HNO_3), trace metals grade or better.

7.19.2 Concentrated hydrochloric acid (HCl), trace metals grade or better.

7.19.3 Reagent water must be produced by a Millipore DI system or equivalent, with a minimum resistivity of 1.0 Mohm/cm at 25 ˚C.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation [1]	Holding Time [2]	Reference
Waters	HDPE	50 mLs	HNO_3, pH < 2;	180 Days	40 CFR Part 136.3

Soils	Glass	3 grams	Cool ≤ 6 °C [3]	180 Days	N/A

[1] Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. If boron or silica are to be determined, plastic containers are preferred. Refrigeration is not required for most programs. Preservation must be verified prior to analysis.

[2] Inclusive of digestion and analysis.

[3] Although ICP analysis of soil does not require refrigeration of the samples, mercury analysis does require refrigeration. Samples which will be used to aliquot volume for both analyses must be refrigerated.

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the TALS Method Comments to determine specific QC requirements that apply.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver Policy DV-QA-003P, *Quality Control Program*.

9.1.2 Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), etc., are described in TestAmerica Denver Policy DV-QA-024P, *QA/QC Requirements for Federal Programs*. DoD QSM 5.0 or 5.1 QC Acceptance Criteria for ICP analyses are presented in Attachment 11. The criteria must be met unless otherwise documented in the project documents.

9.1.3 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via Method Comments in TALS and the Quality Assurance Summaries (QAS) in the public folders.

9.1.4 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.2 Batch Definition

Batches are defined at the sample preparation stage. The batch is a set of up to 20 samples of the same matrix, plus required QC samples, processed using the same procedures and reagents within the same time period. See Policy DV-QA-003P for further details.

9.3 Method Blank

The blank is de-ionized water taken through the procedure as if it were a sample. For soil samples analyzed under the DoD QAPPs, the method blank consists of < 1 mm glass beads that have been processed in the same manner as the samples. A method blank is required with every batch of 20 or less samples.

Acceptance Criteria: The method blank must not contain any analyte of interest above ½ the reporting limit or above one-tenth of the concentration found in the associated samples (for samples with concentrations above the RL).

Corrective Action: If the method blank exceeds allowable levels, all associated samples must be redigested and reanalyzed. A possible exception is the situation in which the analyte is not detected in any of the associated samples, but this can only be done with client approval and it must be addressed in the final report case narrative.

9.4 Laboratory Control Sample (LCS)

The LCS is prepared as described in Section 7.9. One LCS is required with each analytical batch.

Acceptance Criteria: The recovery of the LCS must be within historical control limits. Historical control limits are based on three standard deviations of past results, and must be 80 - 120% or tighter. In the instance where the LCS recovery is greater than 120% and the sample results are < RL, the data may be reported with qualifiers. Such action must be taken in consultation with the client and must be addressed in the report narrative. The process of establishing control limits is described in more detail in the Policy DV-QA-003P. The control limits are stored in TALS.

Corrective Action: If the LCS recovery falls outside of the established limits, all associated samples must be redigested and reanalyzed

9.5 Matrix Spike / Matrix Spike Duplicate (MS/MSD)

MS/MSDs are prepared as described in Section 7.10. One MS/MSD pair is required with each analytical batch. Note that some programs (e.g., North Carolina and South Carolina) require the MS/MSDs to be run at a 10% frequency. Some client specific data quality objectives (DQOs) may require the use of sample duplicates in place of or in addition to MS/MSDs. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing on only the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. Note that if client instructions on the chain of custody form tell the lab to use a field blank for the MS/MSD, this should be double-checked with the laboratory PM.

Acceptance Criteria: The MS and MSD recoveries and the relative percent difference (RPD) between the MS and MSD results must be within the established control limits. Percent recovery control limits are set at ± 3 standard deviations around the historical mean of the LCS recovery data, unless otherwise dictated by the client or project. The RPD control limit is set at 3 standard deviations above the mean of the historical data.

NOTE: DoD QSM 5.0 or 5.1 limits apply to projects performed under this program.

Corrective Actions: The information obtained from MS data are sample/matrix specific and are not normally used to determine the validity of the entire batch. If the MS and/or MSD recovery falls outside of the established control limits, the bracketing CCV and batch LCS recoveries must be within control limits in order to accept results for the associated samples. The following corrective actions are required for MS/MSD recovery failures to rule out lab error:

- Check calculation and instrument performance;
- Verify, if possible, that the MS and MSD were spiked correctly (e.g., very low or very high recoveries);
- Consider objective evidence of matrix interference (e.g., heterogeneous sample, interfering peaks seen on chromatograms, or interference demonstrated by prior analyses);
- Flag the data for any results outside of acceptance limits.
- For any single RPD failure, check calculations; verify, if possible, that the MS and MSD were spiked correctly; check instrument performance; consider objective evidence of matrix interference or sample inhomogeneity; and flag the data.
- If both the parent sample and associated matrix spike results are over range the parent and the spikes shall be diluted by the same amount and the results from the reanalysis reported for both. If the analyte concentration in the parent sample is greater than four times the concentration of spike added, then spike recovery results are not compared to control limits, and the recovery is either reported as “NC” (not calculated) or with a qualifier flag to indicate that the spike was less than four times the analyte concentration in the sample. If the dilution will cause the spike to be less than two times the reporting limit, the MS/MSD do not need to be diluted and the recovery reported as “NC” (not calculated).

- For MS/MSD that serve as batch QC, if the parent sample result is within the calibration range and the MS/MSD results are above the calibration range, the results are reported with the MS/MSD result being flagged as an over-range measurement (e.g., the E-flag qualifier).
- If the MS/MSD are client requested, the parent sample result is within calibration range and the MS/MSD results are above the calibration range, the sample and spike should be diluted, keeping in mind that we need to assess whether or not the dilution will best serve the client's needs. Consult with the PM as needed. Both the parent sample and MS/MSD samples must have the same dilution factor. Some EDDs do not accept data that are at different dilution factors.
- If the native analyte concentration in the MS/MSD sample exceeds 4 times the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated) and the appropriate qualifier flags are added.

NOTE: See Denver Policy Memorandum P16-001 and Corporate Policy Memorandum CA-Q-QM-013 for more detail.

NOTE: Some client programs require reanalysis to confirm matrix interferences. Check special project requirements for this corrective action.

NOTE: This method does not require a sample duplicate. Precision is measured using the MS/MSD. Use of the MS/MSD is preferred as not all samples will contain measurable concentrations of the target analytes. Samples that have target analytes at low concentrations or non-detectable levels do not provide useful precision data. When an MS/MSD is not available, an LCS and LCSD will be used to measure precision. DoD requires the MS/MSD to be assigned by the client. When there is no assigned MS/MSD or there is not enough sample volume provided an LCSD must be prepared.

9.6 Method of Standard Additions (MSA)

9.6.1 This technique involves constructing a calibration curve in the sample matrix itself to compensate for any sample interferents that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences that cause a baseline shift. Attachment 8 provides more guidance on performing MSA analyses.

9.6.2 EPA Method 1311 (Section 8.4) requires that the MSA be used as the calibration method if the MS or MSD recoveries for TCLP extracts are less

than 50% and the sample result is within 80 - 100% of the regulatory level. Attachment 4 provides a list of the regulatory limits. Although the MSA calibration technique may be used with only the sample and a single spiked point, Method 1311 specifies that three spiked points must be used along with the sample.

9.6.3 TALS does not currently have the capability to report results from an MSA-based analysis. If an MSA must be performed, the sample results must be calculated using the MSA spreadsheet (stored at R:\QA\Edit\Forms\Metals\MSA Worksheet - Water) and reported in an NCM. All of the associated samples must then be recalculated against the MSA spreadsheet. The completed spreadsheet must be saved and attached to the analytical batch in TALS along with the raw data.

9.6.4 A manual "N' flag must also be added to all of the affected samples in TALS, indicating the presumptive evidence for the analyte. This flag signals the Project Manager and indicates that narration of the result is required.

9.7 Serial Dilution Test

A dilution test is performed for each batch of samples. The purpose of this test is to ensure that neither positive nor negative interferences are biasing the analytical results. The serial dilution test should be performed on the same sample used to perform the MS/MSD.

Acceptance Criteria: If the analyte concentration is sufficiently high (minimally, a factor of 50 times the MDL), an analysis of a 1:5 dilution (e.g., 1 mL of sample diluted to 5 mL with reagent blank solution) must agree within ± 10% of the original determination. For DoD QSM 5.0 or 5.1 the serial dilution is required if the MS or MSD fails and the parent concentration is greater than 50x the LOQ prior to dilution. 6010D requires the parent sample to be at least 25x higher than the RL to be calculable and sets the recovery limit at 20%.

Corrective Action: If the two results do not agree within the required limits, then a chemical or physical interference is suspected. A qualifier flag is assigned to the data and the failure is addressed in the case narrative to alert the client that a matrix affect may be present. For DoD QSM 5.0 or 5.1 a J-flag is added to the parent sample for the specific analyte if the acceptance criteria are not met.

9.8 Post Digestion Spike (PDS)

Whenever the MS/MSD recoveries are unacceptable, a PDS spike must be performed. The PDS spike is prepared as described in Section 7.10. Some programs (e.g., AFCEE) require a PDS analysis whenever the serial dilution test fails. Other programs (e.g., DoD QSM 5.0 or 5.1) require a PDS to be included in

every batch. Check project requirements. For programs where a PDS is required, the same sample that was used for the serial dilution test should be used for the PDS.

Acceptance Criteria: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 80 - 120% for Method 6010C and 75 - 125% for 6010D.

Corrective Action: If the spike is not recovered within the specified limits, a matrix effect is confirmed. For DoD QSM 5.0 or 5.1 a J-flag is added to the parent sample if the sample concentration is less than 50x the LOQ prior to dilution. Any failures are flagged and should be described in the report case narrative.

9.9 Interference Check Analysis (ICSA / ICSAB)

The ICSA contains only interfering elements, the ICSAB contains analytes and interferents. Refer to Sections 7.5, 7.6, and 7.7 for the preparation of the ICSA and ICSAB solutions. Attachment 4 lists the final concentrations. All analytes are spiked into the ICSAB solution. The ICSA and ICSAB solutions are analyzed at the beginning of the run.

Acceptance Criteria: The ICSAB results for the all analytes must fall within 80-120% of the true value. If any ICSAB analyte result fails criteria, the analysis should be terminated, the problem corrected, the instrument recalibrated, and the samples rerun.

The absolute value of ICSA results for the non-interfering elements must be $\leq$ 2 x RL. The DoD and AFCEE programs have their own criteria based on the version used. For DoD QSM 5.0 or 5.1 the non-spiked analytes must be less than the absolute value of the LOD unless they are verified impurities. For 6010D the non-spiked analytes must be less than the absolute value of the RL.

Corrective action: If the ICSA results for the non-interfering elements do not meet these limits, the field sample data must be evaluated as follows: If the non-interfering element concentration in the ICSA is the result of contamination versus a spectral interference, and this reason is documented, the field sample data can be accepted. The sample data may also be accepted if the affected element was not required. If the interfering elements are not present in the field sample at a concentration which would result in an absolute value > 2x RL, then the field sample data can be accepted. If the interfering element is present in the field sample at a level which would result in a false analyte signal > 2x RL, the data can be accepted only if the concentration of the affected analyte in the field sample is more than 10x the

analyte signal in the ICSA. If the data do not meet the above conditions, then the IECs must be re-evaluated and corrected if necessary and the affected samples reanalyzed.

9.10 Monitoring Internal Standard Results

Yttrium is automatically added as an internal standard (IS) to every solution tested through use of a third pump channel and mixing coil. The analyst must monitor the response of the internal standard throughout the sample analysis run. This information is used to detect potential problems and identify possible background contributions from the sample (i.e., natural occurrence of IS analyte).

Acceptance Criteria: If the internal standard counts fall within ± 30% of the counts observed in the ICAL blank, then the data are acceptable.

Corrective Action: If the internal standard counts in the field samples are outside of the control limits, the field samples must be diluted and reanalyzed;

10.0 Procedure

10.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative.

10.2 Any unauthorized deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

10.3 Sample Preparation

Solid and aqueous samples must be digested prior to analysis by the appropriate method (see SOPs DV-IP-0010 and DV-IP-0015).

10.4 Calibration

10.4.1 Instrument Start Up

Set up the instrument with the operating parameters recommended by the manufacturer. Complete any required preventative maintenance and record in the ICPAES Preventative Maintenance Log. Preventive maintenance recommendations are listed in the TestAmerica Denver Quality Assurance Manual. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required).

10.4.2 Initial Calibration (ICAL)

The calibration curve is established on each day of operation using a blank and one standard. The preparation of the ICAL standards is described in Section 7. The final concentrations of the ICAL standards are presented in Attachment 6. The validity of the calibration curve is confirmed by analysis of the ICV, CCV, ICB, RL Check standard and Low Level ICV/CCV) which are run immediately after the ICAL. Some programs also require a high-level verification check (see Section 10.4.9).

10.4.3 Initial Calibration Verification (ICP ICVH and ICP ICV)

Calibration accuracy is verified using a second-source standard (ICP ICVH and ICP ICV) that is at or below a concentration near the mid-point of the working range. The ICV is analyzed immediately after the ICAL. The preparation of this standard is described in Section 7. The concentration of the ICV standard is presented in Attachment 6.

Acceptance Criteria: The ICV result must fall within 10% of the true value for that solution. The relative standard deviation must be < 5% (the laboratory is using at least two exposures for all ICP analyses).

Corrective Action: If the ICV fails to meet acceptance limits, the standard may be reanalyzed without modification to the instrument operating conditions. Two consecutive, acceptable analyses are required before the analytical run may continue. Otherwise, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified.

10.4.4 Mid Level Continuing Calibration Verification (CCV)

The preparation of the CCV solution is described in Section 7. The final concentrations of the CCVs are presented in Attachment 6. Note that the CCV is made at a different concentration than the ICV to meet NELAC requirements. CCVs are analyzed after the ICV, after every ten samples, and at the end of the analytical run.

Acceptance Criteria: The CCV must be within 10% of the expected value. The relative standard deviation must be <5%.

Corrective Action: If the CCV fails to meet any of these criteria, the standard may be reanalyzed without modification to the instrument operating conditions. *Two consecutive, acceptable analyses are required before the analytical run may continue*. Otherwise, the instrument must be recalibrated and the samples reanalyzed since the last successful CCV must be reanalyzed.

10.4.5 6010C - Low Level Initial Calibration (LLICV) and Continuing Calibration Verification (LLCCV)

The preparation of the LLCCV solution is described in Section 7. The low-level CCV needs to be analyzed at the beginning and end of every run sequence. If low level samples are expected then the low-level CCV should also be run every ten samples.

Acceptance Criteria: The LLCCV must be within +/-30% of the expected value to meet Method 6010C requirements.

Corrective Action: If the LLCCV fails to meet any of these criteria, the standard may be reanalyzed without modification to the instrument operating conditions. *Two consecutive, acceptable analyses are required before the analytical run may continue*. If the calibration cannot be verified within theses specified limits, the analysis of samples containing the affected analytes at similar concentrations cannot continue until the cause is determined and the LLCCV standard successfully analyzed. Otherwise, the instrument must be recalibrated and the samples reanalyzed since the last successful CCV must be reanalyzed. TestAmerica will not hold samples with concentrations greater than 10x the reporting limit to the 30% acceptance criteria.

10.4.6 Initial Calibration Blank (ICB)

System cleanliness is verified by analyzing an ICB after the first CCV. The preparation of the ICB is described in Section 7.

Acceptance Criteria: Absolute values for the calibration blanks must be less than ½ the standard RL. Common lab contaminants such as sodium must be less than the RL. Client specific requirements take precedence. For example, DoD QSM 5.0 or 5.1 requires control of blanks to a concentration less than or equal to the LOD.

Corrective Action: If the ICB fails to meet acceptance limits, a single reanalysis may be attempted without modification to the instrument operating conditions. Otherwise, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified.

10.4.7 RL Calibration Check Standard (ICP CRI)

Calibration accuracy at the RL is verified by analyzing a standard prepared at a concentration at or below the laboratory's standard reporting limit. The preparation of this standard is described in Section 7. Alternate RLSTD

concentrations may be used as necessary to meet client requirements as long as an accurate description of the standard used is entered into the Reagents Module in TALS.

Acceptance Criteria: For routine work the acceptance limits are ± 50% of the expected value. For **6010D and DoD QSM** the acceptance limits are ± 20%.

Corrective Action: If the RL Check standard fails to meet acceptance limits, a single reanalysis may be attempted without modification to the instrument operating conditions. Otherwise, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified.

10.4.8 Lower Limit of Quantitation Check (LLQC)

The lower limit of quantitation check (LLQC) sample should be analyzed after establishing the lower laboratory reporting limits, quarterly and on an as needed basis to demonstrate the desired detection capability. The difference between the LLQC and the LLICV/CCV is that this standard is carried through the entire preparation and analytical procedure. Prepare 7 aliquots spiked at the LLOQ.

Acceptance Criteria: LLQC is verified when all analytes are detected within ± 30% of their true value with an RSD ≤ 20%.

Corrective Action: If the LLQC fails to meet acceptance limits, a single reanalysis may be attempted without modification to the instrument operating conditions. Otherwise, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified.

10.4.9 High-Level Calibration Check Standard

The method 6010C defines the linear working range used for daily analysis based on the LDR studies performed every six months, in which case this standard is not required. However, some programs require verification of the high end of the linear range at different frequencies. The DoD QSM 5.0 OR 5.1 requires that the linear range must be verified on a daily basis. For DoD QSM 5.0 or 5.1 and Method 6010D samples, the spike level of the highest standard analyzed defines the linear range for that day.

Acceptance Criteria: The result for this standard must be within 10% of the expected value.

Corrective Action: If the High-Level Calibration Check standard fails to meet acceptance limits, a single reanalysis may be attempted without modification to the instrument

operating conditions. Otherwise, the analyst must run a standard at a lower concentration until the criteria is met for this calibration or the sample results cannot exceed the level of the highest calibration standard.

10.4.10 Continuing Calibration Blank (CCB)

CCBs, prepared as in Section 7.4, are analyzed after each CCV.

Acceptance Criteria: Absolute values for the calibration blanks must be less than ½ the standard RL. Common lab contaminants such as sodium must be less than the RL. Client specific requirements take precedence. For example, DoD requires control of blanks to a concentration less than or equal to the LOD. Method 6010D sets the CCB upper limit at the RL.

Corrective Action: If the CCB is greater than these limits, a single reanalysis may be attempted without modification to the instrument operating conditions. Otherwise, instrument maintenance should be considered, the calibration re-verified, and all samples analyzed since the last successful CCB must be reanalyzed.

10.5 Sample Analysis

10.5.1 Replicate Readings

The laboratory averages the results from two exposures for Axial and Dual View ICP for each standard, field sample, and QC sample due to sample volume limitations of the autosampler tube.

10.5.2 Rinse Time between Samples

Prior to calibration and between each sample/standard, the system is rinsed with the calibration blank solution. The minimum rinse time between analytical samples is 60 seconds unless, following the protocol outlined in 12.7, it can be demonstrated that a shorter rinse time may be used.

10.5.3 The following analytical sequence is used:

Instrument Calibration
High Standard Verification
ICV
LLICV (6010C only)
CCV
ICB
RL Verification Standard
LLQC (as needed)
ICSA

ICSAB
LRA
CCV
CCB
LLCCV (6010C only)
10 samples
CCV
CCB
LLCCV (6010C)
10 samples
CCV
CCB
LLCCV (6010C)
Repeat sequence with 10 samples between CCV/CCB pairs
CCV
CCB
LLCCV (6010C)

10.5.4 Full method-required QC must be available for each wavelength used in determining reported analyte results. Guidelines are provided in the appendices for minimizing contamination of samples and standards (Attachment 10) and troubleshooting (Attachment 9).

10.5.5 Dilutions for High Levels of Elements of Interest

For 6010, results must fall within the linear range. Dilute and reanalyze all samples for required analytes that exceed the linear range or use an alternate wavelength for which QC data are established. Dilutions must be prepared using the reagent blank solution to maintain the correct acid concentration.

10.5.6 6010D Mid-Run Recalibration

During the course of an analytical run, the instrument may be recalibrated to correct for instrument drift. A recalibration must then be followed immediately by a new analysis of a CCV and CCB before any further samples may be analyzed.

10.5.7 Dilutions for High Levels of Interfering Elements

Dilutions are also required for an element that is included in an IEC calculation if it exceeds the linear range. If a dilution is not performed, the IEC may be inaccurately applied. Therefore, even if an over-range analyte may not be required to be reported for a sample, if that analyte is an interferent for any requested analyte in that sample, the sample must be diluted until the interferent is at or below the working range. An NCM will be written in these instances.

10.6 Instrument Maintenance

See Section 20 in the QAM.

10.7 Troubleshooting

See Attachment 9.

11.0 Calculations / Data Reduction

11.1 Detailed calibration equations can be found in the corporate Policy CA-Q-P-003, *Calibration Curves & Selection of Calibration Points*, and under the public folder, *Arizona Calibration Training*.

11.2 The procedure for performing the calculation of ferric iron is detailed in the Work Instruction WI-DV-0092, *Calculation Methods*.

11.3 ICV percent recoveries are calculated according to the following equation:

$$\%R = \left(\frac{\text{ICV Found Value}}{\text{ICV True Value}} \right) \times 100\%$$

11.4 CCV percent recoveries are calculated according to the following equation:

$$\%R = \left(\frac{\text{CCV Found Value}}{\text{CCV True Value}} \right) \times 100\%$$

11.5 Matrix Spike Recoveries are calculated according to the following equation:

$$\%R = \left(\frac{SSR - SR}{SA} \right) \times 100\%$$

Where:

SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

The relative percent difference (RPD) of a matrix spike/matrix spike duplicate pair is calculated according to the following equation:

$$RPD = \left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2} \right)} \right] \times 100$$

Where:

MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

11.6 The final concentration for a digested aqueous sample is calculated as follows:

$$\text{Final Concentration (mg/L)} = \frac{C \times V1 \times D}{V2}$$

Where:

C = Concentration (mg/L) from instrument readout

D	=	Instrument dilution factor
$V1$	=	Final volume in liters after sample preparation
$V2$	=	Initial volume of sample digested in liters

11.7 The final concentration determined in digested solid samples when reported on a dry weight basis is calculated as follows:

$$\text{Final Concentration (mg/kg), dry weight} = \frac{C \times V \times D}{W \times S}$$

Where:

C	=	Concentration (mg/L) from instrument readout
D	=	Instrument dilution factor
V	=	Final volume in liters after sample preparation
W	=	Weight in kg of wet sample digested
S	=	Percent solids/100

NOTE: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on wet weight basis the "S" factor should be omitted from the above equation.

11.8 The LCS percent recovery is calculated according to the following equation:

$$\%R = \left(\frac{\text{LCS Found Value}}{\text{LCS True Value}} \right) \times 100\%$$

11.9 The IEC's are calculated according to the following equation:

$$IEC = \left(\frac{\text{observed concentration}}{\text{observed concentration of the interfering element}} \right)$$

11.10 The dilution test percent difference for each component is calculated as follows:

$$\%\,Difference = \frac{|I - S|}{I} \times 100$$

Where:

I = Sample result (Instrument reading)

S = Dilution test result (Instrument reading × 5)

Appropriate factors must be applied to sample values if dilutions are performed.

11.11 Documentation and Record Management

11.11.1 All sample data is uploaded to TALS. All sample preparation and analytical batch information, including the batch number(s), list of samples, preparation analyst and date, instrument analyst and date, identification of reagents and standards used, and identification of all measuring equipment used (e.g., balances, thermometers, pipettes) is recorded in TALS.

11.11.2 Raw data is scanned or saved directly as a PDF and is attached to the analytical batch in TALS.

11.12 Reporting

11.12.1 Reporting units are ug/L for water samples and mg/kg for solid samples.

11.12.2 If dilutions were required due to insufficient sample, interferences, or other problems, the reporting limit is multiplied by the dilution factor, and the data may require flagging.

11.12.3 Solid samples are reported on a dry-weight basis unless otherwise requested by the client. Reporting limits are adjusted for both sample size and percent solids.

11.12.4 All associated data are entered or uploaded into the LIMS as required.

NOTE: Unless special instructions indicate otherwise, samples less than the reporting limit are reported as ND.

11.12.5 The initial data review is performed by the analyst and a second-level review is performed by the area supervisor or designee. Both reviews are documented on a Data Review Checklist. See SOP DV-QA-0020 for more detail on the review process. Any manually transcribed data must be reviewed in its entirety by the second level data reviewer.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. An initial method detection limit study is performed in accordance with Policy DV-QA-005P. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method or program requirements require a greater frequency. For DoD and DOE projects, an MDL verification is performed quarterly. DoD QSM 5.0 or 5.1 requires the MDLV spike level to be 2 - 4 times the calculated MDL.

12.2 Limit of Quantitation Verification (LOQV)

The verification of the limit of quantitation (LOQ or LLOQ) is performed quarterly for work performed according to the DOD/DOE QSM 5.0 or 5.1. A blank matrix is spiked at 1-2 the laboratory RL and carried through the entire preparation and analytical procedures. Recoveries are assessed based on historical limits.

12.3 Instrument Detection Limit Study

12.3.1 Instrument detection limit (IDL) studies are conducted quarterly for each instrument and each wavelength used for analysis.

12.3.2 Run seven blanks on three non-consecutive days.

12.3.3 Calculate the standard deviation for each day. The final IDL concentration is the average of the three daily standard deviation values.

12.3.4 See Policy DV-QA-014P for a discussion of IDL studies and evaluation of IDL results.

12.3.5 For Method 6010D the IDL solutions:

- Should be prepared with each of the different matrices analyzed on the instrument;
- Should be prepared with 10 replicates for each matrix;
- Should have all the replicates for each matrix analyzed in a single day.

12.4 Linear Dynamic Range (LDR)

12.4.1 The LDR must be determined initially (i.e., at initial setup) and then every three months for each analyte wavelength used on each instrument. The linear range is the concentration above which results cannot be reported without dilution of the sample.

12.4.2 The LDR must be determined from a linear calibration prepared in the normal manner using the normal operating procedures described in Sections 10 and 11.

12.4.3 The LDR is determined by analyzing successively higher standard concentrations of the analyte. A minimum of three standards is required for the initial and on-going studies, and one of the levels must be close to the upper end of the range. The highest concentration must be within 10% of the stated concentration.

12.4.4 The highest standard that meets this criterion defines the maximum concentration that can be reported for sample analysis without dilutions. Certain programs do not allow the use of LDRs for reporting purposes and instead require all sample results to fall below the highest daily standard analyzed.

12.4.5 If the instrument is adjusted in any way that may affect the LDRs, new dynamic ranges must be determined. The LDR data must be documented and kept on file.

12.5 Background Correction Points

12.5.1 To determine the appropriate location for off-line background correction when establishing methods, the user must scan the area on either side adjacent to the wavelength of interest and record the apparent emission intensity from all other method analytes. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations.

12.5.2 Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Background correction points must be set prior to determining IECs. Refer to the ICP instrument manual for specific procedures to be used in setting background correction points.

12.6 Interelement Corrections (IECs)

12.6.1 ICP interelement correction (IEC) factors must be determined prior to the analysis of samples and every six months thereafter. If the instrument is adjusted in any way that may affect the IECs, the IECs must be re-determined.

12.6.2 When initially determining IECs for an instrument, wavelength scans must be performed to ensure that solutions in use are free from contaminants. If an IEC varies significantly from the previously determined IEC, then the possibility of contamination should be investigated. The purity of the IEC check solution can be verified by using a standard from a second source or an alternate method (i.e., GFAA or ICP-MS). Published wavelength tables (e.g., MIT tables, Inductively Coupled Plasma-Atomic Spectroscopy: Prominent Lines) can also be consulted to evaluate the validity of the IECs.

12.6.3 Refer to the facility-specific instrument operation SOP and instrument manufacturer's recommendations for specific procedures to be used in setting IECs. An IEC must be established to compensate for any interelement interference which produces a false analytical result with an absolute value greater than the RLs shown in Attachment 1. Note that the USACE program requires a control limit of 2x |MDL|, which is feasible when verified MDLs are used.

12.6.4 To determine IECs, run a single element standard at the established linear range. To calculate an IEC, divide the observed concentration of the analyte by the observed concentration of the "interfering element." Method 6010D requires that the IEC standards include Al, B, Ba, Ca, Cu, Fe, Mg, Mn, Mo, Na, Ni, Se, Si, Sn, V, and Zn.

12.6.5 Dual-View ICP IECs are more sensitive to small changes in the plasma and instrument setup conditions. Adjustments in the IECs will be required on a more frequent basis for the CID detector instruments as reflected by the ICSA response.

12.7 Rinse Time Determination

12.7.1 Rinse times must be determined annually.

12.7.2 To determine the appropriate rinse time for a particular ICP system, a standard containing the highest concentration level that would be reported for samples is aspirated as a regular sample followed by the analysis of a series of rinse blanks. The length of time required to reduce the analyte signals to < RL will define the rinse time for a particular ICP system.

12.7.3 For some analytes it may be impractical to set the rinse time based on the linear range standard result (i.e., analyte not typically detected in environmental samples at that level and an excessive rinse time would be required at the linear range level).

12.7.4 Rinse time studies can be conducted at additional concentration levels. These additional studies must be documented and kept on file if a concentration other than the linear range level is used to set the rinse time. The concentration levels used to establish the rinse time must be taken into consideration when reviewing the data.

12.7.5 The ICP instruments use an intelligent rinse program. The intelligent rinse lengthens the rinse time whenever a sample result for a known problem analyte is above a set concentration.

12.8 Demonstration of Capabilities

12.8.1 All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually.

12.8.2 IDOCs and on-going proficiency demonstrations are conducted as follows: Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample is typically the LCS spike level. The results of the IDOC study are summarized in the NELAC format, as described in SOP DV-QA-0024. IDOCs are approved by the Quality Assurance Manager and the Technical Director. IDOC records are maintained by the QA staff in the central training files.

12.8.3 If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

12.9 Training Requirements

The Group Leader is responsible for ensuring that this procedure is performed by an associate who has been properly trained in its use and has the required experience. A new analyst must be working under documented supervision prior to approval of the IDOC. Documentation that a new analyst is performing under supervision must

be entered into the batch record (View Batch Information) until that analyst's IDOC has been approved by the QA Manager (or designee). See requirements for demonstration of analyst proficiency in SOP DV-QA-0024.

13.0 Pollution Control

13.1 It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, order chemicals based on quantity needed, and prepare reagents based on anticipated usage and reagent stability).

13.2 Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards and reagents requiring disposal.

14.0 Waste Management

14.1 All waste will be disposed of in accordance with federal, state, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in Section 13, *Waste Management and Pollution Prevention*, of the Corporate Safety Manual, and DV-HS-001P, *Waste Management Plan*.

14.2 The following waste streams are produced when this method is carried out:

14.2.1 Acid solutions from ICP drain - Waste Stream J

14.2.2 Metals waste potentially contaminated with Cat 1 radioactive materials – Waste Stream RJ

Note: Radioactive, mixed waste and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Radioactive Waste Coordinator for proper management of radioactive or potentially radioactive waste generated by this procedure.

15.0 References / Cross-References

15.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Third Edition and all promulgated updates, EPA Office of Solid Waste, through January 2008.

15.1.1 Method 6010C, Revision 3, Update IV, February 2007.

15.1.2 Method 6010D, Revision 4, Update V, July 2014.

15.2 Department of Defense Quality Systems Manual for Environmental Laboratories, Final Version 4.2, 10/25/2010.

15.3 Department of Defense Quality Systems Manual for Environmental Laboratories Version 5.0, July 2013.

16.0 Method Modifications:

Item	Method	Modification
1	EPA 6010C	This procedure uses mixed calibration standard solutions purchased from approved vendors instead of using individual mixes prepared in house as recommended by the subject methods.
2	EPA 6010C	The alternate run sequence presented in Section 10.5.3 is consistent with method requirements. Additional QC (i.e., ICSA) analyses were added to accommodate the CLP protocol requirements.
3	EPA 6010C	Method 6010 states that if the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a specific "concentration range around the calibration blank." Because of the lack of definition for "concentration range around the calibration blank," the laboratory has adopted the procedure in EPA CLP ILMO4.0 for determining IECs,
4	EPA 6010C	Section 9.9 of Method 6010C states: "If less than acceptable accuracy and precision data are generated, additional quality control tests are recommended prior to reporting concentration data for the elements in this method." The dilution test helps determine if a chemical or physical interference exists. Because the laboratory sometimes does not have prior knowledge if the MS/MSD will be within criteria, the analyst may select to perform a dilution test on one sample in each preparation batch. According to the method, the post digestion spike (PDS) determines any potential matrix interferences. In this procedure, matrix interference is determined by evaluating data for the LCS, MS/MSD, and serial dilutions. The laboratory must request documented, clear guidance when an unusual matrix will be received for a project and a request to perform the dilution test or PDS on a client-identified sample.

17.0 Attachments

Attachment 1 Metals Analyzed by ICP and Reporting Limits
Attachment 2 Matrix Spike and Aqueous Laboratory Control Sample Levels
Attachment 3 Low Level ICV and CCV Spiking Levels
Attachment 4 Interference Check Sample Concentrations
Attachment 5 TCLP Reporting Limits, Regulatory Limits and Matrix Spike Levels
Attachment 6 6500 Initial Calibration &Continuing Calibration Verification Standards
Attachment 7 Summary of Quality Control Requirements
Attachment 8 MSA Guidance
Attachment 9 Troubleshooting Guide
Attachment 10 Contamination Controls
Attachment 11 DoD QSM 5.0 or 5.1 QC Acceptance Criteria

18.0 Revision History

Revision 6, dated 31 July 2017
- Annual review
- Added reference to QSM 5.1 throughout SOP where applicable
- Updated spiking amounts in Section 7.12.2 to be based off 1L instead of 500ml
- Added LCSD requirement to Section 9.5 for DoD when not enough volume for MS/MSD
- Added Section 11.12 regarding reporting requirements
- Added current Section 12.2 regarding LOQVs

Revision 5, dated 31 July 2016
- Annual review
- Minor formatting and language corrections throughout
- Removed references to AFCEE and USACE
- Added Section 3.8 reagent water definition
- Added six-month expiration for intermediate standards in Section 7.2.2
- Added clarification to Section 7.3.2 regarding new standard verification
- Added new Section 7.18 explaining daily LR standard
- Removed cooling requirement for water samples in Section 8.0
- Added information to MS/MSD Section 9.5 to reflect current policy
- Changed Section 9.9 to Section 9.6, renumbered other sections accordingly
- Added information to Section 9.6 regarding the MSA requirement for TCLP extract samples
- Created subsections 9.6.1 - 9.6.4
- Added language to Section 10.4.9 to clarify daily linear range requirements
- Added Section 11.2 referencing the ferric iron work instruction
- Added requirement to review all manually transcribed data at second level review (Section 11.11.3)
- Archived pre-2011 revision histories

Revision 4, dated 31 December 2015
- Added requirements for Method 6010D to the SOP
- Minor grammar and formatting corrections throughout
- Added list of IEC test analytes to Section 12.5.4
- Added Section 10.5.6 regarding mid-run recalibration
- Added Section 12.2.5 defining 6010D IDL studies

Revision 3, dated 31 July 2015
- Annual review
- Updated Section 7.4 for how to make the 5% HNO_3/5% HCl solution
- Updated Section 12.2 for MDLV spike level to 2-4x MDL
- Updated Section 12.8.2 to use LCSs instead of ICVs for the DOC
- Reformatting throughout
- Removed reference to silica holding time
- Added Maintenance and troubleshooting sections
- Replaced Section 11.10 to match current practice
- Removed Section 12.2
- Removed Sections 1.3.1 and 1.3.2
- Added new Section 1.6
- Removed reference to glass beads in Section 6.2
- Corrected Reagent and Standard formulae throughout to agree with current practice

Revision 2, dated 31 July 31 2014
- Annual review
- Updated Section 6.1.3 to specify purity of argon gas
- Added statement to section 9.1.2 to reference DoD QSM 5.0 criteria in Attachment 11
- Removed references to preparation of oil/oily samples throughout the document as the lab no longer supports this digestion method
- Added references for prep methods to section 15
- Added DOD QSM 5.0 QC acceptance criteria as Attachment 11

Revision 1, dated 15 July 2013
- Annual review
- Removed section 1.7
- Added section 3.8
- Corrected formatting
- Added section 11.12
- Removed Attachment 8, renumbered attachments and fixed references to attachments throughout the document

Revision 0.3, dated 13 July 2012
- Annual Review
- Clarified soil preservation for ICP only analysis, Section 8
- Updated section 9.1, 10.1, 10.2, and 12.1 to reflect current practice
- Updated sections 10.4.6 and 10.4.10 to control calibration blanks to ½ the RL

Revision 0.2, dated 30 June 2011
- Added reference to DV-IP-0017 “Microwave Digestion” throughout document
- Added section 6.3 “Computer Software and Hardware”
- Removed Uranium from the ICSA/ICSAB tables in sections 7.4, 7.5, and 7.6
- Updated sections 7.14 and 7.15 to reflect current practices
- Updated the Acceptance Criteria in sections 9.4, 9.6, and 9.10
- Referenced the TestAmerica Denver Quality Assurance Manual in section 10.4.1
- Updated section 11 to reference corporate SOP CA-Q-S-005, “Calibration Curves” and Arizona Calibration Training spreadsheet
- Added IEC calculation to section 11

Earlier revision histories have been archived and are available upon request.

Attachment 1

Metals Analyzed by ICP and Reporting Limits

ELEMENT	Symbol	CAS #	6010 Analyte	Reporting Limit (µg/L) Water	Reporting Limit (mg/kg) Soil
Aluminum	Al	7429-90-5	X	100	10
Antimony[trace]	Sb	7440-36-0	X	10	1
Arsenic[trace]	As	7440-38-2	X	15	1
Barium	Ba	7440-39-3	X	10	1
Beryllium	Be	7440-41-7	X	1	0.1
Bismuth	Bi	7440-69-9		100	10
Boron	B	7440-42-8	X	100	10
Cadmium[trace]	Cd	7440-43-9	X	5	0.5
Calcium	Ca	7440-70-2	X	200	20
Chromium	Cr	7440-47-3	X	10	1
Cobalt	Co	7440-48-4	X	10	1
Copper	Cu	7440-50-8	X	15	2
Iron	Fe	7439-89-6	X	100	10
Lead[trace]	Pb	7439-92-1	X	9	0.8
Lithium	Li	7439-93-2	X	10	5
Magnesium	Mg	7439-95-4	X	200	20
Manganese	Mn	7439-96-5	X	10	1
Molybdenum	Mo	7439-98-7	X	20	2
Nickel	Ni	7440-02-0	X	40	4
Phosphorus	P	7723-14-0	X	3,000	300
Potassium	K	7440-09-7	X	3,000	300
Selenium[trace]	Se	7782-49-2	X	15	1.3
Silicon	Si	7631-86-9		500	50
Silver[trace]	Ag	7440-22-4	X	10	1
Sodium	Na	7440-23-5	X	1	100
Strontium	Sr	7440-24-6	X	10	1
Sulfur	S	7704-34-9	X	200	2
Thallium[trace]	Tl	7440-28-0	X	15	1.2
Thorium	Th	7440-29-1		15	15
Tin	Sn	7440-31-5	X	100	10
Titanium	Ti	7440-32-6	X	10	1
Uranium	U	7440-61-1		60	20
Vanadium	V	7440-62-2	X	10	2
Zinc	Zn	7440-66-6	X	20	2
Zirconium	Zr	7440-67-7		15	1

Attachment 2

Matrix Spike and Aqueous Laboratory Control Sample Levels

ELEMENT	LCS Level (µg/L)	Matrix Spike Level (µg/L)
Aluminum	2,000	2,000
Antimony	500	500
Arsenic	2,000	2,000
Barium	2,000	2,000
Beryllium	50	50
Bismuth	2,000	2,000
Boron	1,000	1,000
Cadmium	50	50
Calcium	50,000	50,000
Chromium	200	200
Cobalt	500	500
Copper	250	250
Iron	1,000	1,000
Lead	500	500
Lithium	1,000	1,000
Magnesium	50,000	50,000
Manganese	500	500
Molybdenum	1,000	1,000
Nickel	500	500
Phosphorous	10,000	10,000
Potassium	50,000	50,000
Selenium	2,000	2,000
Silicon	10,000	10,000
Si (as SiO_2)	21,400	21,400
Silver	50	50
Sodium	50,000	50,000
Strontium	1,000	1,000
Sulfur	2,000	2,000
Thallium	2,000	2,000
Thorium	2,000	2,000
Tin	2,000	2,000
Titanium	1,000	1,000
Uranium	2,000	2,000
Vanadium	500	500
Zinc	500	500
Zirconium	500	500

Attachment 3

Low Level ICV/CCV

ELEMENT	LCS Level (µg/L)
Aluminum	100
Antimony	10
Arsenic	15
Barium	10
Beryllium	1
Bismuth	100
Boron	100
Cadmium	5
Calcium	200
Chromium	10
Cobalt	10
Copper	15
Iron	100
Lead	9
Lithium	10
Magnesium	200
Manganese	10
Molybdenum	20
Nickel	40
Phosphorous	3,000
Potassium	3,000
Selenium	15
Silicon	500
Si (as SiO_2)	1070
Silver	10
Sodium	1,000
Strontium	10
Thallium	15
Thorium	15
Tin	10
Titanium	10
Uranium	60
Vanadium	10
Zinc	20
Zirconium	15

Attachment 4

Interference Check Sample Concentrations

Element	ICSA (µg/L)	ICSAB (µg/L)
Aluminum	500,000	500,000
Antimony	-	1,000
Arsenic	-	2,000
Barium	-	500
Beryllium	-	500
Bismuth	-	1,000
Boron	-	2,000
Cadmium	-	1,000
Calcium	500,000	500,000
Chromium	-	500
Cobalt	-	500
Copper	-	500
Iron	200,000	200,000
Lead	-	1,000
Lithium	-	1,000
Magnesium	500,000	500,000
Manganese	-	500
Molybdenum	-	1,000
Nickel	-	1,000
Phosphorous	-	2,000
Potassium	-	50,000
Selenium	-	5,000
Silicon	-	10,000
Silica	-	21,400
Silver	-	1,000
Sodium	-	50,000
Strontium	-	1,000
Sulfur	-	1,000
Thallium	-	10,000
Titanium	-	1,000
Vanadium	-	500

Attachment 4

Interference Check Sample Concentrations (cont'd)

Element	ICSA (µg/L)	ICSAB (µg/L)
Zinc	-	1,000
Tin	-	10,000
Thorium	-	10,000
Uranium	2,000	2,000
Zirconium	-	1,000

Attachment 5

TCLP Reporting Limits, Regulatory Limits and Matrix Spike Levels

ELEMENT	Reporting Level (µg/L)	Regulatory Limit (µg/L)	Spike Level (µg/L)
Arsenic	500	5000	4000
Barium	10000	100000	12000
Cadmium	100	1000	1100
Chromium	500	5000	5200
Lead	500	5000	5500
Selenium	250	1000	3000
Silver	500	5000	1050
Copper	100	N/A	2250
Zinc	200	N/A	2500

Attachment 6

6000 Dual View Calibration, ICV & CCV Standards

Element	Calibration Level	ICV (µg/L)	CCV (µg/L)
Aluminum Lo	1,000	250	500
Aluminum Hi	100,000	40,000	50,000
Antimony	2,000	250	1,000
Arsenic	2,000	250	1,000
Barium	1,000	250	500
Beryllium	1,000	250	500
Bismuth	2,000	500	1000
Cadmium	1,000	250	500
Calcium	10,000	2,000	5,000
Chromium	1,000	250	500
Cobalt	1,000	250	500
Copper	1,000	250	500
Iron Lo	5,000	250	2,500
Iron Hi	100,000	80,000	50,000
Lead	2,000	250	1000
Magnesium	40,000	10,000	20,000
Manganese	1,000	250	500
Molybdenum	1,000	250	500
Nickel	1,000	250	500
Phosphorous	2,000	2,000	1,000
Potassium	100,000	20,000	50,000
Selenium	2,000	500	1,000
Silver	1,000	250	500
Sodium Lo	10,000	2000	5,000
Sodium Hi	500,000	40,000	250,000
Strontium	1,000	250	500
Sulfur	10,000	4,000	5,000
Thallium	2,000	500	1,000
Thorium	10,000	3,000	5,000
Tin	2,000	500	1,000
Vanadium	1,000	250	500
Uranium	20,000	5,000	10,000
Zinc	1,000	250	500
Zirconium	1,000	250	500

Attachment 7
Summary Of Quality Control Requirements

QC Parameter	Frequency	Acceptance Criteria	Corrective Action
Two-point Initial Calibration	Beginning of every analytical run, every 24 hours, whenever instrument is modified, or CCV criterion is not met	RSD between multiple exposures ≤5%	Terminate analysis; Correct the problem; Prepare new standards; Recalibrate following system performance.
ICV	Beginning of every analytical run.	90 - 110 % recovery.	Terminate analysis; Correct the problem; Recalibrate.
CCV	After the ICV, after every 10 samples and at the end of the run.	90-110% recovery	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV.
RL Standard	At the beginning of the run	Results must within 50%	Terminate analysis; Correct the problem; Recalibrate.
LLICV/CCV	At the beginning of the run and after every 10 samples	Recovery must be within 30%	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable LLCCV.
ICB	Beginning of every analytical run, immediately following the initial CCV.	The result must be within +/- ½ RL from zero.	Terminate analysis; Correct the problem; Recalibrate.
CCB	Immediately following each CCV (except for the CCV following the ICV).	The result must be within +/- ½ RL from zero.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB.
ICSA	Beginning of every run	See Section 9.10	See Section 9.10
ICSAB	Immediately following each ICSA.	Results must be within 80 - 120% recovery.	See Section 9.10
Dilution Test	One per prep batch.	For samples > 10x LOD (after dilution)' dilutions must agree within 10%.	Narrate the possibility of physical or chemical interference per client request.

See Section 10.5.3 for run sequence to be followed.

Attachment 7

Summary of Quality Control Requirements (Continued)

QC Parameter	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	One per sample preparation batch of up to 20 samples.	The result must be less than or equal to ½ the RL. Sample results greater than 10x the blank concentration are acceptable. Samples for which the contaminant is < ½ RL may not require redigestion or reanalysis (see Section 9.3)	Re-run once in a clean tube. If > ½ RL, re-digest and reanalyze samples. Note exceptions under criteria section. See Section 9.4 for additional requirements.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	LCS must be within 80 - 120% recovery or in-house control limits. Samples for which the contaminant is < RL and the LCS results are > 120% may not require redigestion or reanalysis (see Section 9.4)	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS.
Matrix Spike (MS)	One per sample preparation batch of up to 20 samples.	75 – 125% recovery or tighter in-house control limits.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added.
Matrix Spike Duplicate (MSD)	One per sample preparation batch of up to 20 samples. 10% frequency for some programs (see 9.5)	75 – 125 % recovery; RPD ≤ 20% or tighter in-house control limits.	See Corrective Action for Matrix Spike.

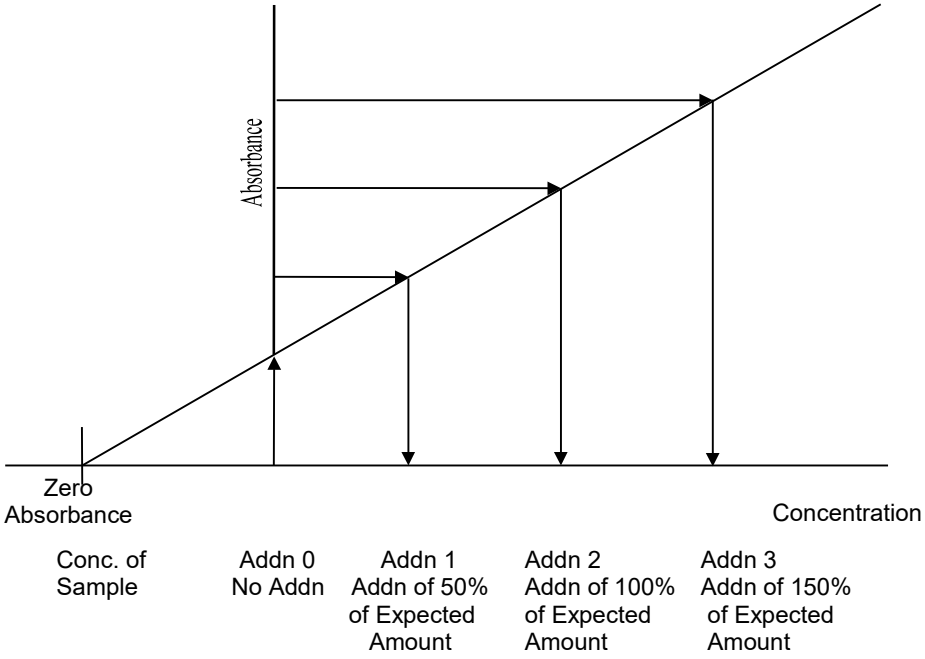
Attachment 8

MSA Guidance

Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked standard should be the same.

In order to determine the concentration of analyte in the sample, the analytical value of each solution is determined and a plot or linear regression performed. On the vertical axis the analytical value is plotted versus the concentrations of the standards on the horizontal axis. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the absolute value of the point of interception of the horizontal axis is the concentration of the unknown.



For the method of standard additions to be correctly applied, the following limitations must be taken into consideration:

- The plot of the sample and standards must be linear (r=0.995 or greater) over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.
- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

Attachment 9

Troubleshooting Guide

Problem	Possible Cause/ Solution
High Blanks	Increase rinse time Clean or replace tip Clean or replace torch Clean or replace sample tubing Clean or replace nebulizer
Instrument Drift	RF not cooling properly Vacuum level is too low Replace torch (Crack) Clean or replace nebulizer (blockage) Check room temperature (changing) Replace pump tubing Room humidity too high Clean torch tip (salt buildup) Check for argon leaks Adjust sample carrier gas Replace RF generator
Erratic Readings, Flickering Torch or High RSD	Check for argon leaks Adjust sample carrier gas Replace tubing (clogged) Check drainage(back pressure changing) Increase uptake time (too short) Increase flush time (too short) Clean nebulizer, torch or spray chamber Increase sample volume introduced Check that autosampler tubes are full Sample or dilution of sample not mixed Increase integration time (too short) Realign torch Reduce amount of tubing connectors
Standards reading twice normal absorbance or concentration	Incorrect standard used Incorrect dilution performed

Attachment 10

Contamination Control Guidelines

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered gloves should not be used in the metals laboratory because the powder contains silica and zinc as well as other metallic analytes.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

The following are helpful hints in the identification of the source of contaminants:

Yellow pipette tips and volumetric caps can sometimes contain cadmium.

Some sample cups have been found to contain lead.

The markings on glass beakers have been found to contain lead. If acid baths are in use for glassware cleaning, they should be periodically checked for contaminants since contaminant concentrations will increase over time.

New glassware especially beakers can be a source of silica and boron.

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Latex gloves contain over 500 ppb of zinc.

Attachment 11
DoD QSM 5.0 OR 5.1 QC Criteria for Analysis by ICP

QSM 5.0 OR 5.1 Table 8. Inorganic Analysis by ICP	
Requirement	**DoD QSM 5.0 OR 5.1 and DOE QSAS 3.0**
Linear Dynamic Range (LDR) or high-level standard check	Run an LDR or high-level check standard at least once every 6 months. When calibrating with a single standard and a blank, the daily LDR standard must be analyzed at a concentration greater than any samples analyzed that day. Data cannot be reported above the high calibration range without an established/passing high-level check standard. Must be within ± 10% of expected value. Dilute samples within the calibration range or re-establish/verify the LDR.
Initial Calibration (ICAL)	Measure a minimum of one high standard and a calibration blank, daily. If more than one standard used, then $r^2 \geq 0.99$ ($r \geq 0.995$), otherwise no acceptance criteria. The ICAL must pass before running any samples. NOTE: The laboratory currently performs duplicate burns for the ICPAES method.
Initial Calibration Verification (ICV)	Run second-source standard once after each ICAL and prior to sample analysis. All reported analytes must be within ± 10% of expected value. Correct any problems, verify standard, and rerun ICV. If that fails, correct problem and rerun ICAL. Verification must pass before running any samples.
Continuing Calibration Verification (CCV)	Run CCV after every 10 field samples, and at the end of the analysis sequence. All reported values within ± 10% of expected value If the CCV is above the project acceptance limits and there are no detections in the samples, TestAmerica will report the non-detect results with a case narrative comment in addition to applying any data qualifier flags required by the project (3HR). Correct any problems then rerun CCV. If that fails, then repeat ICAL. Reanalyze all samples since last successful CCV. Results cannot be reported without a valid CCV. Or Immediately (within one hour) analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails, take corrective action(s) and re-calibrate; then reanalyze all affected samples since the last acceptable CCV. If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analytes(s) in all samples since the last acceptable CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Low-Level Calibration Check Standard (Low-level ICV)	Run low-level standard at a concentration ≤ LOQ daily after one-point ICAL. All reported analytes must be within ± 20% of expected value. Correct any problems, then reanalyze or repeat ICAL. Results cannot be reported without a valid low-level calibration check standard.

Attachment 11
DoD QSM 5.0 OR 5.1 QC Criteria for Analysis by ICP
(continued)

QSM 5.0 OR 5.1 Table 8. Inorganic Analysis by ICP	
Requirement	**DoD QSM 5.0 OR 5.1 and DOE QSAS 3.0**
Initial and Continuing Calibration Blank (ICB.CCB)	Analyze calibration blank before analyzing samples, after every 10 field samples, and at the end of the analysis sequence. No analytes detected > ½ LOQ (RL) or >1/10 the amount measured in any sample or 1/10 the regulatory limit, whichever is greater. (13ICP) If not accepted by client, ICB/CCB must be <LOD. If criteria not met, correct problem If reanalysis is not possible, apply B-flag to all results for the specific analyte(s) in all samples processed with the contaminated blank. Must be explained in the case narrative. Flagging is only appropriate when samples cannot be reanalyzed. Correct any problems and repeat ICAL. All samples following the last acceptable calibration blank must be reanalyzed. CCB failures due to carryover may not require an ICAL.
Interference Check Solution (ICS)	Run the ICS at the beginning of an analytical run (after ICAL and prior to sample analysis). ICS-A: Absolute value of concentration for all non-spiked analytes must be < LOD (unless they are a verified trace impurity from one of the spiked analytes). ICS-AB: Within ± 20% of expected value. (Note: ICS-AB not needed if instrument can read negative responses.) Correct any problems and reanalyze ICS. Do not analyze samples without a valid ICS. NOTE: TAL Denver has a letter from the ICSA standards manufacturer for many of the elements.
Method Blank	One per prep batch. No analytes detected > ½ LOQ (RL) or >1/10 the amount measured in any sample or 1/10 the regulatory limit, whichever is greater. Common lab contaminants not detected > LOQ. (2CLC) For ICP, common lab contaminants are: Al, Ca, Fe, K, Mg, Na, Si, Zn (Ba for TCLP) If criteria not met, correct problem. If required, reprep and reanalyze MB and all samples processed with the contaminated blank. If reanalysis is not possible, apply B-flag to all results for the specific analyte(s) in all samples processed with the contaminated blank. Must be explained in the case narrative. Flagging is only appropriate when samples cannot be reanalyzed.
LCS	One per prep batch. Recovery must meet DoD QSM limits. If the LCS recovery is above the project acceptance limits and there are no detections in the samples, TestAmerica will report the non-detect results with a case narrative comment in addition to applying any data qualifier flags required by the project (3HR). Correct any problems, then re-prep and reanalyze LCS and associated samples for failed analytes in all samples in the associated batch. If corrective action fails, apply Q-flag to specific analyte(s) in all samples in associated batch.

Attachment 11
DoD QSM 5.0 OR 5.1 QC Criteria for Analysis by ICP
(continued)

QSM 5.0 OR 5.1 Table 8. Inorganic Analysis by ICP	
Requirement	**DoD QSM 5.0 OR 5.1 and DOE QSAS 3.0**
Matrix Spike (MS)	One MS per prep batch. Use DoD acceptance criteria for LCS. If MS fails, consult project-specific DQOs and contact client to see if additional measures need to be taken. For specific analyte(s) in parent sample, apply J-flag if acceptance criteria are not met. If MS falls outside LCS limits, evaluate data to determine the source of the difference and to determine if there is a matrix effect or analytical error.
MSD or Sample Duplicate	Analyze one MSD or sample duplicate per prep batch per matrix. RPD between duplicates must be ≤ 20%. For failures, consult project-specific DQOs and contact client for additional measures to be taken. If acceptance criteria are not met, apply J-flag. If MS falls outside LCS limits, evaluate data to determine the source of the difference and to determine if there is a matrix effect or analytical error.
Dilution Test	One per prep batch if MS or MSD fails. Only applicable for samples with concentrations >50x LOQ (prior to dilution). For samples with lower concentrations perform PDS. Five-fold dilution must agree within ± 10% of the original result. Apply J-flag if acceptance criteria not met and explain in the case narrative.
Post-Digestion Spike (PDS) Addition	Perform Recovery Test when dilution test fails or analyte concentration in all samples is <50 x LOQ. Recovery must be within 80-120 % of expected result. If test fails, then run samples by MSA or apply J-flag to all sample results (for same matrix) in which MSA was not run when recovery is outside of 80 - 120%.
Method of Standard Additions	When dilution or post digestion spike fails and if required by the project. Document use of MSA in case narrative.

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